Energy transport pathways in photosynthetic antennas

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2012

Summary

Photosynthesis is a biological process by which organisms such as plants, algae, and certain bacteria use sunlight to produce energy-rich organic compounds and oxygen using water and carbon dioxyde. Research on photosynthesis is important because it would help devising artificial systems to employ solar energy in a clean and efficient fashion. This would be a solution to the urgent need of renewable sources of energy in our society. The first step of photosynthesis is absorption of light; light-harvesting antennas are protein complexes dedicated to this task. When light is absorbed by exciting a pigment molecule in the antennas, its excitation energy can be transferred between pigments. This excitation energy eventually reaches the reaction center where chemical processes are run. The aim of the research in this thesis is to quantitatively characterize the energy pathways between pigments in light-harvesting antennas.

An important light-harvesting antenna of plants is LHCII in the photosystem II of the chloroplast. Chapter 5 illutrates an exciton model for LHCII based on its crystal structure, Redfield-Förster theories, and experimental data. Energy transfer in LHCII is described by a number of electronic excitations which, instead of changing the electronic configuration of individual chlorophylls, are delocalized over a number of interacting chlorophylls (excitons). This picture is complicated by disorder of the chlorophyll energies and electronic couplings between chlorophylls, which adds a degree of randomization on transfer dynamics and energy pathways. The chapter describes in detail how excitations migrate between clusters of coupled chlorophylls to reach the low-energy chlorophyll clusters in the three monomers of LHCII.

The other chapters of this thesis report experimental studies. The main experimental technique employed is transient absorption or pump-probe spectroscopy. To mimic the effect of sunlight, the samples containing antennas suspended in solution are illuminated with a one-color laser pulse (the pump beam). The color (i.e. the energy) of the excitation determines what pigment molecules (e.g. chlorophylls, carotenoids, bilins, etc.) and what electronic states are excited. A second white-light beam (the probe beam) is used for detecting whether the excited pigments absorb or emit light at a certain energy. This yields information on the excited states at a certain time after excitation. Further analysis of the experimental data allows extraction of the averaged lifetimes governing the decay

of the excited states or the transfer of excitations to the next pigment molecules.

In addition to LHCII, photosytem II also hosts the three minor antennas CP24, CP26, and CP29. The structures of CP24 and CP26 are known to share some degree of homology with the structure of LHCII but are still unresolved at the time of writing. In chapter 2 the focus is on transfer between chlorophylls, whereas in chapter 3 we show how carotenoids transfer light excitation to the chlorophylls. The amount of transfer from carotenoids to chlorophylls *b* or chlorophylls *a* is different in the two antennas studied. Carotenoid to chlorophyll transfer is observed from the S2 and the vibrationally "hot" S1 excited states. On the other hand it is found that the S1 excited state of carotenoids is not active in energy transfer. From the experimental results we conclude that the structure and the functioning of CP26 is substantially similar to that of monomeric LHCII, except for the functional disruption of the "bottleneck" chlorophylls *a*604 and *b*605. CP24, on the other hand, differs substantially from the other antennas. In particular, the chlorophylls absorbing at 670 nm attributed to Chl *a*602 and/or *a*603 are found to mediate a large part of the transfer to the chlorophylls *a* at low energies.

In chapter 6 LHCII was studied using polarized transient absorption spectroscopy. This method is effective in resolving chlorophyll bands at the same energies which are obscured in standard pump-probe spectroscopy. It is found that the initially polarization is lost in 3.3-3.5 picoseconds. This phenomenon occurs due to the angle between the chlorophylls transitions at 652-662 nm excited by the pump beam and the final chlorophyll acceptors, and also due to equilibration between the three monomers of LHCII.

The subject of chapter 4 is the light-harvesting antenna phycocyanin 645 of the unicellular alga *Chroomonas* CCMP270. This alga populates relatively deep waters and has evolved into an efficient light harvester. Experiments with several excitation colors were needed to unambiguously identify the pathway of energy through the eight bilin molecules that bind to phycocyanin 645.

Finally, chapter 7 investigates the opposite phenomenon to light harvesting, i.e. how LHCII dissipates light energy in order to protect the plant from excess sunlight. For the experiments LHCII antennas were incorporated in an acrylamide gel matrix to prevent aggregation. Subsequently, the LHCII antennas were switched into a dissipative state. It is shown that the energy of chlorophylls *a* are transferred to the low-lying S1 state of a carotenoid, whereby the energy can be dissipated as heat. The study confirms that carotenoids are involved in the photoprotection of plants.